Process for the decorative design of a lacquered substrate surface

The invention relates to a process for the decorative design of a lacquered substrate surface and also to the substrates obtained in accordance with the process. The process according to the invention may find application, in particular, in the decorative surface design of vehicle bodies, of the components thereof and also of vehicle parts.

Diverse examples of decorative surface designs are known, in particular, from the domain of automobile lacquering. These include, for example, individual lacquer finishes, for example effect-producing lacquer finishes, lacquer finishes in special colour tones or lacquer finishes in the form of images, patterns or ornaments, but also the application of appropriately designed adhesive films.

DE-C-196 13 383 describes a shaping punch with which microstructures can be applied onto objects. For example, microstructures for generating a destructive interference can be impressed into a lacquer layer which has been applied onto a television picture tube for the purpose of eliminating reflection.

The object of the invention is the provision of a process for the decorative design of a lacquered substrate surface. In this connection the process is to permit the generation of unique and impressive decorative effects, for example in the domain of the lacquering of goods that are manufactured industrially or by handicraft, such as, for example, sports equipment, instrument casings, and in particular in the domain of vehicle lacquering and vehicle-part lacquering. It has been shown that this object can be achieved by

virtue of the process for the decorative design of a substrate surface, which constitutes a subject of the invention and which is characterised in that a curable coating agent is applied onto the substrate surface and one or more embossing dies are pressed, in each case with their side exhibiting a relief characterised by amplitude maxima that are spaced from one another in the range from 100 to 20,000 nm, into the uncured coating layer at the place or places to be decorated, whereupon at least the regions that are covered by the embossing die or dies are at least partially cured, thereafter the embossing die or dies is/are removed and, in case places are present in the coating layer that are not yet cured, these are completely cured.

The process can be implemented with coating agents that are capable of being cured by high-energy radiation such as light and/or that are capable of being cured thermally, whereby curing may be effected by irradiation and/or thermally.

Accordingly, a first, preferred embodiment of the invention relates to a process for the decorative design of a substrate surface, which is characterised in that a coating agent which is capable of being cured by irradiation with high-energy radiation, e.g. with light, is applied onto the substrate surface and one or more partially or totally translucent embossing dies is/are pressed, in each case with its/their side exhibiting a relief characterised by amplitude maxima that are spaced from one another in the range from 100 to 20,000 nm, into the uncured coating layer at the place or places to be decorated, whereupon at least the regions that are covered by the embossing die or dies are irradiated through the embossing die or dies with high-energy radiation, e.g. with light having a wavelength from 180 to 1,000 nm, thereafter the embossing die or dies is/are removed and, in case places are present in the

coating layer that are not yet cured, these are cured by high-energy radiation, in particular photochemically.

A second embodiment of the invention is a process for the decorative design of a substrate surface, characterised in that a coating agent which is capable of being cured by thermal means is applied onto the substrate surface and one or more embossing dies is/are pressed, in each case with its/their side exhibiting a relief characterised by amplitude maxima that are spaced from one another in the range from 100 to 20,000 nm, into the uncured coating layer at the place or places to be decorated, whereupon at least the regions that are covered by the embossing die or dies are at least partially cured thermally, thereafter the embossing die or dies is/are removed and, in case places are present in the coating layer that are not yet cured, these are completely cured thermally.

It is to be understood that the first, preferred embodiment and the second embodiment which are described above can also be combined with one another to create further embodiments by appropriate coating agents which are suitable for this purpose being used and, for example, a) being firstly cured photochemically and, after removal of the embossing dies, places that are not yet cured being cured thermally, optionally in addition photochemically or b) being firstly cured thermally and, after removal of the embossing dies, places that are not yet cured being cured photochemically, optionally in addition thermally or c) being firstly cured photochemically and thermally and, after removal of the embossing dies, places possibly present that are not yet cured being cured photochemically and/or thermally. If photochemical and thermal curing are utilised in one process step, combined with one another, this may be undertaken in sequence or simultaneously. Hereinafter, for the purpose of simplification with respect to the embossing die or dies and the place or places to be

decorated, the plural will be used in each case. At this point it should be pointed out that the expression "place or places to be decorated" also includes the special case of a substrate surface to be decorated over its full area.

~~Without giving a binding explanation, it is assumed by way~~ of theoretical clarification that the decorative effect, arising for the observer, of the surfaces that have been designed using the process according to the invention arises substantially as a result of diffraction of light and interference on the structures which are generated by means of the embossing dies in the surface of the coating layer which is generated from the curable coating agent. For the observer the places that are provided with the embossing dies during the at least partial curing give rise to differing optical effects, depending on the viewing angle; the observer perceives these effects as decorative ~~elements.~~

The process according to the invention is suitable for the decorative design of a coating layer, for example on industrially manufactured goods such as, e.g., cladding panels, furniture, instrument casings, household appliances, sports equipment, e.g. skis, surfboards, in particular automobile bodies and the components thereof as well as vehicle parts generally. For example, in the case of the coating layer to be decoratively designed it may be a question of a single-layer lacquer or of a coating layer which is visible to the observer and which is applied within the scope of a multilayer lacquering. The goods that are provided with the coating layer may themselves be made for example of wood, glass, but in particular of metal or plastic and optionally already be prelayered with one or more lacquer layers.

The curable coating agents that are used in the process according to the invention are not subject to any restriction; it may be a question of all conventional

coating agents, which may be aqueous, diluted with solvents or free of solvents and water. They may also be pulverulent.

In the case of the first, preferred embodiment of the process according to the invention, use is made of coating agents that are capable of being completely cured by irradiation with high-energy radiation, e.g. with light. They are not subject to any restriction, they may be aqueous, diluted with solvents or preferably free of solvents and water. In the case of the coating agents that are capable of being completely cured by irradiation with light it is a question, in particular, of the cationically and/or radically curing coating agents which are known to a person skilled in the art. Radically curing coating agents are preferred. In the course of the influence of high-energy radiation on coating layers which have been applied from these coating agents, radicals arise in the coating layers which trigger a cross-linking of the coating layers by radical polymerisation of olefinic double bonds.

The preferred, radically curing coating agents contain prepolymers, such as polymers or oligomers, which exhibit radically polymerisable olefinic double bonds, in particular in the form of (meth)acryloyl groups in the molecule. The prepolymers may be present in combination with conventional reactive diluents - i.e. reactive liquid monomers.

Examples of prepolymers or oligomers are (meth)acrylic-functional (meth)acrylic copolymers, epoxy resin (meth)acrylates, polyester (meth)acrylates, polyether (meth)acrylates, polyurethane (meth)acrylates, unsaturated polyesters, unsaturated polyurethanes or silicone (meth)acrylates with number-average molecular masses (Mn) preferably in the range from 200 to 10,000, in particularly preferred manner from 500 to 3,000 and with, on average, 2

to 20, preferably 3 to 10, radically polymerisable, olefinic double bonds per molecule.

If use is made of reactive diluents, they are employed in amounts from 1 to 50 wt.%, preferably from 5 to 30 wt.%, relative to the total weight of prepolymers and reactive diluents. It is a question of low-molecular, defined compounds which may be mono-unsaturated, di-unsaturated or polyunsaturated. Examples of such reactive diluents are: (meth)acrylic acid and the esters thereof, maleic acid and the half-esters thereof, vinyl acetate, vinyl ether, substituted vinyl ureas, ethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate, 1,3- and 1,4-butanediol di(meth)acrylate, vinyl (meth)acrylate, allyl (meth)acrylate, glycerol tri(meth)acrylate, glycerol di(meth)acrylate, glycerol mono(meth)acrylate, trimethylolpropane tri(meth)acrylate, trimethylolpropane di(meth)acrylate, trimethylolpropane mono(meth)acrylate, styrene, vinyltoluene, divinylbenzene, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipropylene glycol di(meth)acrylate, tripropylene glycol di(meth)acrylate, hexanediol di(meth)acrylate, as well as mixtures thereof.

The preferred, radically curing coating agents may contain conventional photo-initiators, e.g. in amounts from 0.1 to 5 wt.%, preferably from 0.5 to 3 wt.%, relative to the sum of radically polymerisable prepolymers, reactive diluents and photo-initiators. Examples of photo-initiators are benzoin and benzoin derivatives, acetophenone and acetophenone derivatives, e.g. 2,2-diacetoxyacetophenone, benzophenone and benzophenone derivatives, thioxanthone and thioxanthone derivatives, anthraquinone, 1-benzoylcyclohexanol, organophosphoric compounds such as, e.g., acyl phosphine oxides. The photo-initiators may be employed on their own or in combination. In addition, further synergistic components, e.g. tertiary amines, may

be employed.

In the case of the second embodiment the thermally curable coating agents may contain conventional binding-agent systems that are capable of being cured by addition reactions and/or condensation reactions and/or by radical or cationic polymerisation and that, optionally in addition, are physically drying. In the case of the addition reactions and/or condensation reactions in the aforementioned sense it is a question of lacquer-chemistry cross-linking reactions which are known to a person skilled in the art, such as, for example, the ring-opening addition of an epoxide group onto a carboxyl group accompanied by formation of an ester group and a hydroxyl group, the addition of a hydroxyl group onto an isocyanate group accompanied by formation of a urethane group, the reaction of a hydroxyl group with a blocked isocyanate group accompanied by formation of a urethane group and elimination of the blocking agent, the reaction of a hydroxyl group with an N-methylol group accompanied by elimination of water, the reaction of a hydroxyl group with an N-methylol ether group accompanied by elimination of the etherification alcohol, the transesterification reaction of a hydroxyl group with an ester group accompanied by elimination of the esterification alcohol, the transurethanation reaction of a hydroxyl group with a carbamate group accompanied by elimination of alcohol, the reaction of a carbamate group with an N-methylol ether group accompanied by elimination of the etherification alcohol.

If a combination of photochemical and thermal curing is to be effected, then the coating agents which in themselves are capable of being cured by irradiation with light, according to a radical mechanism, may additionally contain, besides the photo-initiators, conventional radical initiators that are capable of being activated thermally

and that, starting from 40 to 120°C, for example, are able to form radicals. Examples of thermolabile radical initiators are: organic peroxides, organic azo compounds or C-C cleaving initiators. The preferred amounts required are between 0.1 to 5 wt.%, relative to the sum of radically polymerisable prepolymers, reactive diluents and radical initiators.

A further possible way of combining photochemical and thermal curing consists in making use of coating agents which are only capable of being partially cured by irradiation with light and which contain a mixture consisting of, for example, 50 to 99 wt.% of a binding-agent system that is capable of being cured by irradiation with light and 1 to 50 wt.% of a binding-agent system that is capable of being cured by addition reactions and/or condensation reactions and that, optionally in addition, is physically drying, whereby the wt.% figures refer in each case to the solids and make up 100 wt.%, and/or in making use of binding-agent systems which in themselves are capable of being cured by irradiation with light and which exhibit additional groups that are capable of cross-linking as a result of addition reactions and/or condensation reactions. Examples of addition reactions and/or condensation reactions are those already mentioned above.

The curable coating agents that are used in the process according to the invention may be pigmented or coloured-transparent or colourless-transparent. It is preferably a question of colourless clear lacquers or of colour-imparting and/or effect-imparting coating agents, e.g. basecoat lacquers.

The coating agents may be applied by conventional methods, for example by spray application, onto the substrates to be decorated. Application may be effected onto the entire

substrate surface or onto one or more partial areas thereof or only onto the points of the substrate surface to be decorated, for example to a dry-layer thickness from 5 to 250 µm.

After the application and a flash-off phase or fusion phase which is optionally provided, the embossing dies are pressed, in each case with their side exhibiting a relief characterised by amplitude maxima that are spaced from one another in the range from 100 to 20,000 nm, preferably from 800 to 20,000 nm, into the uncured coating layer at the places to be decorated.

The embossing dies may consist fundamentally of any materials that are suitable for the application according to the invention, for example of metal, glass or plastic. It may be a question of opaque or partially or totally translucent embossing dies. The partially or totally translucent embossing dies that are used in particular in the case of the first, preferred embodiment may consist of glass or, preferably, of transparent plastics, for example polyester, polycarbonate, polystyrene, poly(meth)acrylate or silicone plastic. Flexible, optionally elastic plastic is preferred. In the case of the embossing dies it may be a question of mouldings which can be used as punches, or it may be a question of films which are pressed into the uncured coating layer at the places to be decorated, for example with the aid of a punch exhibiting an unstructured, smooth surface or with the aid of an appropriate roller. The films may be structured as such or they may exhibit a structured coating. In order to alleviate their release from the places to be decorated after the at least partial curing, the embossing dies may expediently be specially finished on their side exhibiting a relief. This finish may consist, for example, in the embossing-die material as such exhibiting non-stick properties, for example by reason

of appropriate provision of additives, or the embossing-die surface may be provided with a non-stick coating.

The embossing dies exhibit on one side a relief characterised by amplitude maxima that are spaced from one another in the range from 100 to 20,000 nm, preferably from 800 to 20,000 nm. The relief may be opaque or, particularly in the case of the first, preferred embodiment, may exhibit regions of differing translucence, e.g. it may be totally translucent or partially translucent. Generation of the relief may be effected, for example, by mechanical processes such as engraving or embossing and/or by standard processes of microstructure technology, for example photolithographic processes, vapour deposition, microprinting technology or laser-assisted technologies, which are optionally combined with etching technologies. The reliefs may, for example, exhibit depressions, elevations and/or holes.

In the case of the reliefs which are present on one side of the embossing dies and which are characterised by amplitude maxima that are spaced from one another in the range from 100 to 20,000 nm, preferably from 800 to 20,000 nm, it is a question, for example, of those with an amplitude height in the range, for example, between 100 and 5,000 nm. The amplitude maxima as such may be present in the form of points, lines or flat, inclined plateaus and/or plateaus exhibiting depressions. In the case of amplitude maxima that are present as plateaus the spacing figure from 100 to 20,000 nm, preferably from 800 to 20,000 nm, between the amplitude maxima refers to the spacing between adjacent plateau edges or between a plateau edge and adjacent amplitude maxima which are present as points or lines. The relief may exhibit irregular structures or it may be a question of regular structures such as optical diffraction gratings, for example cross gratings or, in the simplest case, optical line gratings. The grid lines may in this

connection be arranged in non-equidistant or equidistant manner. In the case of amplitude maxima of varying height the spacing refers to the spacing resulting from the top view.

The side of the embossing dies that, in each case, exhibits the relief may take up arbitrary surface areas, for example from a few square centimetres to a few square metres. In this connection the relief as such may take up the entire area of the side of the embossing dies exhibiting the relief, i.e. the relief and the side exhibiting the relief are identical and coincide in contour and surface area. The relief as such may, however, constitute only a part of the area of the side of the embossing dies exhibiting the relief, whereby the external contour line of the relief may coincide with the external contour line of the side exhibiting the relief. The part of the area of the embossing die that does not exhibit a relief may be translucent or opaque. Diverse design possibilities arise for the side of the embossing dies exhibiting the relief. For example, the side of the embossing dies exhibiting the relief may exhibit a relief frame and, optionally within the relief frame, further reliefs which are likewise bounded by contour lines. Individual reliefs bounded by contour lines may in this connection be arranged parallel in a common plane or in different, vertically offset planes or individual reliefs may deviate, for example, up to an angle of a maximum of 10 degrees from this parallel arrangement. By reason of the various possibilities for variation in the design of the side of the embossing dies exhibiting the relief, an extremely wide range of decorative elements can be generated at the places to be decorated, for example images, ornaments, patterns, logos, symbols, initials, type marks, etc.

According to the invention the embossing dies are pressed, as already described above, into the uncured coating layer

at the places to be decorated. Thereafter the uncured coating layer is at least partially cured. In this connection, in the case of the first, preferred embodiment, irradiation is effected with high-energy radiation, for example with light having a wavelength from 180 to 1,000 nm, through the embossing dies which have been pressed into the lacquer, or in the case of the second embodiment, heating is effected, for example to temperatures from 20 to 180°C, preferably from 40 to 160°C.

Besides light, electron radiation, for example, may also be employed by way of high-energy radiation. For this purpose, use may be made of conventional electron emitters which are familiar to a person skilled in the art.

In the case of irradiation with light, use may be made, for example, of monochromatic or polychromatic light. It is preferably a question of ultraviolet light. Preferred are UV beam sources with emissions in the wavelength range from 180 to 420 nm, in particularly preferred manner from 200 to 400 nm. Preferred examples of UV beam sources are optionally doped, high-pressure, medium-pressure and low-pressure mercury radiators, gas-discharge tubes such as, e.g., xenon low-pressure arc lamps, black-light tubes, UV flash lamps.

The practical implementation and also technical details of the irradiation are known to a person skilled in the art and require no further elucidation. For example, the duration of irradiation lies within the range of the duration of an UV flash from, for example, 1 millisecond to 5 minutes, depending on the irradiation process used and the type of the UV radiation sources. Preferred is a duration of irradiation, i.e. an actual period of exposure to the UV radiation, of less than 5 minutes.

After the at least partial curing of the places to be decorated, the embossing dies are removed from the places to be decorated.

If places are present in the coating layer that are not yet cured, these are cured after the removal of the embossing dies, in the case of the first, preferred embodiment by irradiation, in particular photochemically, and in the case of the second embodiment, thermally. "Places in the coating layer that are not yet cured" may be present, for example, if use has been made of a coating agent that can be cured exclusively by photochemical means and a radiation dose that is not sufficient for complete curing has acted upon the coating layer or if use has been made of a coating agent that can be cured exclusively by thermal means and a thermal action on the coating layer that is sufficient for curing has not taken place or, in the case of the aforementioned combination of photochemical and thermal curing, for example, places that are not yet cured have been cured firstly only photochemically and, after removal of the embossing dies, thermally, or conversely.

In the case of the first, preferred embodiment, for example, the expression "places in the coating layer that are not yet cured" also encompasses those places which have not been reached by the radiation in the course of the irradiation through the embossing dies, for example because use has been made of embossing dies that are only partially translucent and/or regions of the coating layer situated outside the embossing dies were covered up during the irradiation.

An exclusive photochemical curing of places in the coating layer that are not yet cured comes into consideration when, according to the first embodiment, use has been made of a coating agent that is capable of being completely cured by irradiation (e.g. with light) for the purpose of producing

the coating layer. Where use has been made of a coating agent that is capable of being cured exclusively by thermal means according to the second embodiment, a thermal curing of places that are not yet cured takes place, for example at temperatures between 20 and 180°, preferably between 40 and 160°C. The choice of the conditions in the course of the thermal curing conforms, for example, to the composition of the coating agent in question or to the type of the substrates to be decorated. The same applies to photochemical curing.

Subsequent to the process according to the invention a clear-lacquer layer consisting of an arbitrary clear-lacquer coating agent or an arbitrary transparent plastic film can be applied onto the decorated places or onto the entire lacquered substrate surface. In particular in connection with the application of a conclusive clear-lacquer layer, the process according to the invention can be employed as a separate process step in a process for producing a multilayer lacquer finish. For example, the lacquer layers exhibiting decorative elements are applied using the process according to the invention onto unlacquered substrates or onto substrates that have been precoated with a single-layer or multilayer lacquer finish and are provided with a conclusive clear-lacquer layer. In this connection the procedure may be such that the aforementioned curing, serving to achieve the decorative effect, of places in the coating layer that are not yet cured is effected jointly with the curing of the conclusive clear-lacquer layer by photochemical or thermal means, depending on the type of the clear-lacquer coating agent which was used for generating the conclusive clear-lacquer layer.

The process according to the invention may preferably be implemented in such a way that a clear-lacquer coating agent is applied by way of curable coating agent onto dark,

e.g. black, substrates or darkly lacquered, e.g. black-lacquered, substrates. This is because the achievable effect according to the invention can be perceived in particularly intense manner on dark undersurfaces. It is also possible to make use of a colour-imparting and/or effect-imparting coating agent, e.g. a basecoat-lacquer coating agent, by way of curable coating agent, which is preferably darkly pigmented, in particularly preferred manner pigmented black.

With the process according to the invention, lacquered substrate surfaces can be provided with decorative elements which display an effect that is dependent on the viewing angle. Deviating from the light/dark flop and/or coloured flop which is dependent on the viewing angle and which is known from the domain of effect lacquering, for example metallic lacquering, with the process according to the invention decorative elements can be generated which exhibit a new kind of viewing-angle-dependent flop effect, a so-called "on/off" or "phantom" flop. This conceptual terminology is intended to make it clear that it is a question here of a flop effect which is characterised by a viewing-angle-dependent perceptibility or non-perceptibility of the decorative elements or parts thereof. This is because, from the viewpoint of the observer, the alternation between perception and non-perception of the decorative elements may occur abruptly and without fluid transitions. Perception of the decorative elements only obtains over a certain viewing-angle range. Within this perception-angle range the decorative elements show up to the human eye, e.g. in all the visible spectral colours.

If the decorative elements have been generated by means of embossing dies with a relief exhibiting irregular structures, then the decorative elements are perceptible as a holographic image showing up in, e.g., all the spectral colours. If the decorative elements in the simplest case

have been generated by means of an embossing die with a relief that is present as an optical line grating, then the decorative elements are perceptible in the form of a continuous spectrum, e.g. a spectrum exhibiting all the spectral colours, i.e. a rainbow-like effect arises for the observer.

The process according to the invention can also be employed for the partial-area and hence decorative, more or less strong attenuation of the reflectance behaviour (elimination of reflections) of external lacquer-coating layers, which in themselves are glossy, on substrates. The embossing dies then exhibit a relief that is suitable for generating destructive interferences in the coating layer.

With the process according to the invention, lacquered substrate surfaces can be decoratively designed in impressive manner. The process according to the invention can be employed in particularly advantageous manner e.g. in the motor-vehicle domain, which includes both the design of motor vehicles and of motor-vehicle parts in the handicraft domain and in the industrial domain of initial finishing, in particular also, for example, as an integrated process step within the scope of the initial lacquering of automobiles. In the case of initial finishing it may, for example, be a question of a decorative design of the entire visible external surface of a motor vehicle, of parts within the interior space of a motor vehicle or a question of an individual customised decorative design, for example the appending of initials of the customer, etc, or it may be a question of a mass-production decorative design, for example the appending of a company logo, of a type mark or the decorative accentuation of edges or transitions between various regions of a body, for example also between vehicle parts adjoining one another, etc. In the handicraft domain it may likewise be a question, for example, of a decorative design of the entire visible external surface of a motor

vehicle, of parts within the interior space of a motor vehicle or an individual customised decorative design of a vehicle or of a vehicle part or a question of a repair of motor vehicles or motor-vehicle parts which have already been decoratively designed in appropriate manner. The process according to the invention may be carried out in the handicraft domain, for example in a lacquering workshop as a separate process step or as an integrated process step within the scope of an entire or partial lacquering.

The invention is elucidated in more detail in the following.

Example

A metal test plate (5 cm by 10 cm) coated with a commercial black basecoat lacquer is coated with a solvent-free UV-curable clear lacquer having a 100 % solids content to a wet-layer thickness of 100 µm. A 3-mm-thick glass plate which exhibits on one side a line grating generated by chromium vapour deposition and making up a mask area of 2 cm by 2 cm (width of the grid lines taking the form of a plateau: 8 µm, amplitude height of the grid lines: 120 nm, equidistant spacing of the external edges of the plateau: 8 µm) is pressed with its side exhibiting the line grating into the uncured clear-lacquer layer. Thereafter the entire clear-lacquer layer which is partially covered by the glass plate is irradiated with an UV flash lamp (3,500 Watt seconds) with 5 UV flashes at intervals of 4 seconds. After this, the glass plate is removed and the clear-lacquer layer which, in part, is still uncured is irradiated analogously with 5 UV flashes. In the event of top-view observation in white light, a region with a size of 2 cm by 2 cm is perceived in the clear-lacquer surface as a spectrum exhibiting rainbow colours. When the metal test plate is tilted, as from a certain viewing angle the

rainbow-coloured region is suddenly no longer perceived.